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Spectrophotometric kinetic estimation of alditols in acidic medium

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ABSTRACT

The kinetic method for estimation of alditols by cerium (IV) in acidic medium has been investigated spectrophotometrically at 360nm under pseudo-first order condition. The reaction was first order with respect to substrate and oxidant. The estimation has been done from the calibration plots obtained by using pseudo first order rate constant of the indicator reaction and also by fixed time and fixed absorbance method. The rate data was obtained for the indicator reaction under varying kinetic experimental conditions. Results of this study indicate that the estimated values for the simulated samples are consistent and reproducible with in ~ ±1%.

Key words: Kinetic estimation, alditols, first order reaction, acidic medium, Cerium.

INTRODUCTION

Kinetic studies have been used as a tool to know the mechanism of a reaction. Kinetics provides the most important indirect evidence in the mechanism. The metal ion oxidants have been widely employed in synthetic chemistry[1-2] including carbohydrate chemistry[3-6]. These are stable inexpensive and can readily be stored and handled. Kinetic method of analysis have been widely developed and accepted in chemical analysis of different samples[7-9]. Alditols are acyclic, polyhydric alcohols, that are wide spread in nature, particularly in lower forms of life. Amongst hexitols, D-Sorbitol and D-Mannitol have various medical applications and both have the same molecular formula($C_6H_{14}O_6$). Both these hexitols are used in chewing gum, chocolate, Ice creams, Pharmaceutical & nutritional tablets.The kinetic and mechanistic studies of these hexitols with metal oxidants Manganese[10], Rhodium[11-12] have been reported. The present work describes the preliminary procedure for the estimation of alditols with Ce(IV) in sulphuric acid medium.

MATERIALS AND METHODS

Materials:

Commercially available chemicals of pure quality were used without further purification. Stock solution of alditols(D-sorbitol and D-mannitol) were prepared in double distilled water. Ce^{IV} stock solution were prepared by dissolving Ceric sulphate (Loba chemie) in aqueous sulphuric acid.Systronics-104 visible spectrophotometer was used.

Kinetic Method:

The kinetic runs were performed in stoppered glass vessels in a controlled temperature(± 0.1°C) water bath. The kinetics of redox reaction between alditols (D-sorbitol and D-mannitol) and cerium(IV) in sulphuric acid medium was followed under pseudo first order condition by measuring absorbance at 360nm at constant temperature. The unknown is calculated in simulated sample by fixed time method and fixed absorbance method from the regression equations.

RESULTS AND DISCUSSION

Indicator Reaction- The reaction followed first order kinetics upto 2 half lives. The rate increased with the first power of concentrations of alditols,sulphuric acid, hydrogen ion, bisulphate ion.These indicator reactions between alditols and cerium(IV) in sulphuric acid medium under the kinetic run conditions can be represented as in eq.(1).

$$C_6H_{14}O_6 + 12Ce(IV) + 6H_2O \longrightarrow 6HCOOH + 6H^+ + 12Ce(III)$$

The formation of formic acid was confirmed by usual spot test and now by paper chromatography and HPLC methods.

Kinetic estimation- The rate of these indicator reactions under the present kinetic conditions in terms of disappearance of cerium(IV) with time at constant temperature and sulphuric acid concentration can be given by

$$\frac{-d[Ce^{IV}]}{dt} = k_0\,[\text{ cerium(IV)}]_0\,[\text{ alditol}]_0 = k_{obs}\,[\text{ }Ce^{IV}]_0 \qquad \text{------(2)}$$

Thus when $[\text{alditol}]_0 >> [\text{ }Ce^{IV}]_0$

Then,

$$k_{obs} = k_0\,[\text{ alditols}] \qquad \text{-------(3)}$$

Eq.(2) alternatively expressed as eq.(4) for the finite change in the initial concentration of cerium(IV) in a given fixed time interval.

$$\frac{-\Delta[Ce^{IV}]}{\Delta t} = k_0\,[Ce^{IV}]_0\,[\text{alditols}]_0 \quad \text{------(4)}$$

The initial concentration of cerium(IV) i.e. $[Ce^{IV}]_0$ is kept constant in each kinetic run with varying initial concentration of alditols i.e.$[\text{alditols}]_0$, therefore

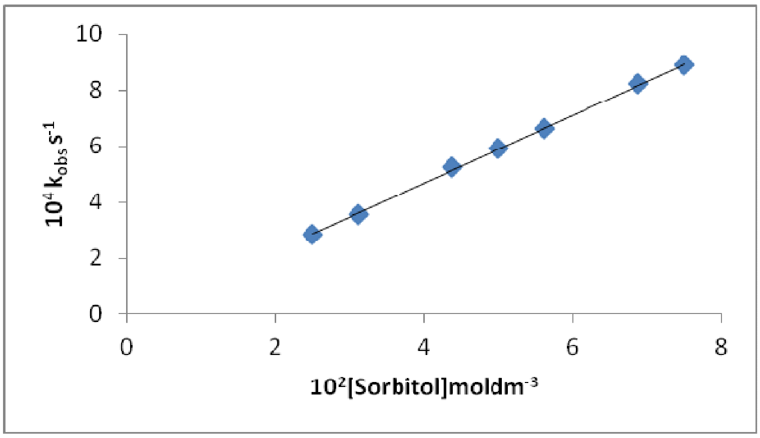
$$\frac{-\Delta[Ce^{IV}]}{\Delta t} = k_0\,[\text{alditols}]_0 \quad \text{------(5)}$$

Equation 3 & 5 have been used to obtain the following different three calibration plots to determine the concentrations (D-sorbitol & D-mannitol) of simulated samples of alditols.

- k_{obs} and [alditol].
- Absorbance i.e.$[Ce^{IV}]_0$ and $[\text{alditol}]_0$ at fixed time intervals.
- Time in seconds and [alditol]0 at fixed absorbance i.e. at fixed concentration of $[Ce^{IV}]_0$.

The kinetic data of variation of k_{obs} , [Fig.1(a), (b)] absorbance at fixed time interval [Fig.2(a), (b)] and time at fixed absorbance with initial concentration of alditol [Fig.3(a), (b)] in different kinetic run are given graphically for D-Sorbitol and D- Mannitol.

D-Sorbitol Vs k_{obs}



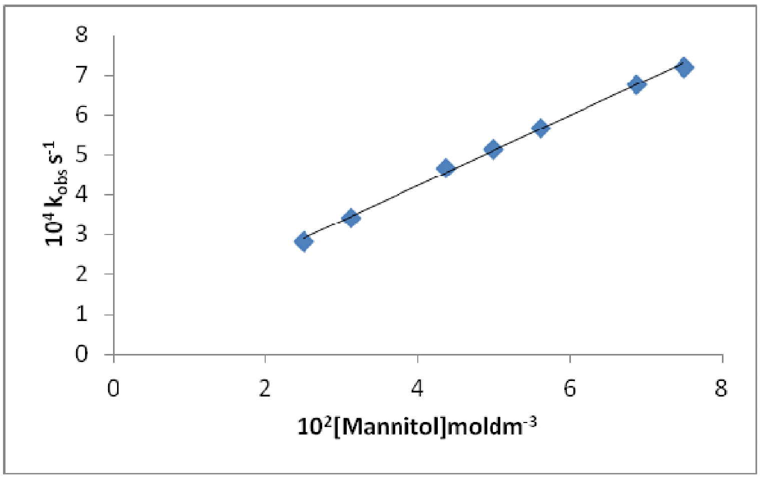
10^4 k_{obs} = 1.213[D-sorbitol]- 0.167 Corr. Coeff. = 0.99

Result: 10^2[Unknown-1](moldm^{-3}) = 3.77(calcd.): 3.75(actual)

10^2[Unknown-2](moldm^{-3}) = 6.24(calcd.): 6.25(actual)

(a) Estimation of D-Sorbitol

D-Mannitol Vs k_{obs}



10^4 k_{obs} = 0.878[D-Mannitol]+ 0.703 Corr. Coeff. = 0.99

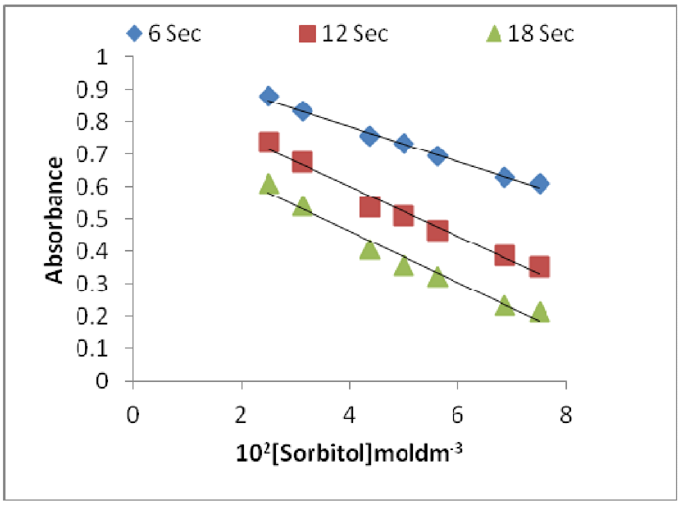
Result: 10^2[Unknown-1](moldm^{-3}) = 3.77(calcd.): 3.75(actual)

10^2[Unknown-2](moldm^{-3}) = 6.20(calcd.): 6.25(actual)

(b) Estimation of D-Mannitol

Fig.1 Estimation of alditols by variation of kobs with [alditol]. 10^4[Ce^{IV}] = 2.5 moldm^{-3}; [H_2SO_4] = 0.7moldm^{-3}; Temp.= 296K ; λ = 360nm.

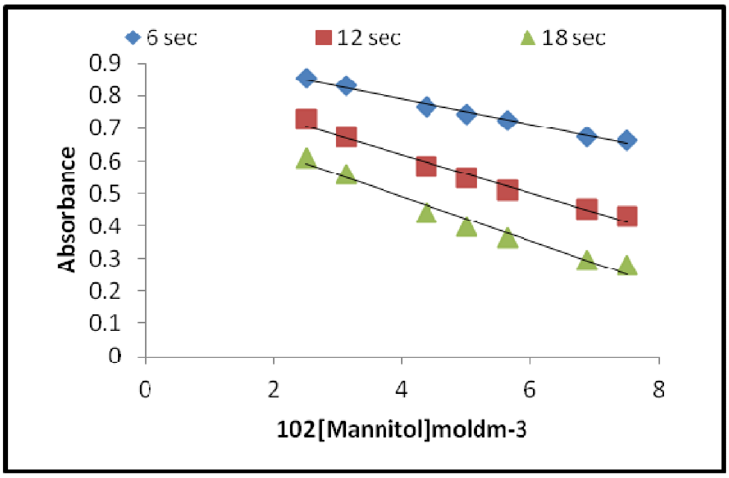
D-Sorbitol Vs Absorbance



A_6 = - 0.054[D-Sorbitol]+ 1.003 Corr. Coeff. = 0.99
A_{12} = - 0.076[D-Sorbitol]+ 0.905 Corr. Coeff. = 0.97
A_{18} = - 0.080[D-Sorbitol]+ 0.783 Corr. Coeff. = 0.97
Result: 10^2[Unknown-1](moldm^{-3}) = 3.76(calcd.): 3.75(actual)
10^2[Unknown-2](moldm^{-3}) = 6.26(calcd.): 6.25(actual)

(a) Estimation of D-Sorbitol

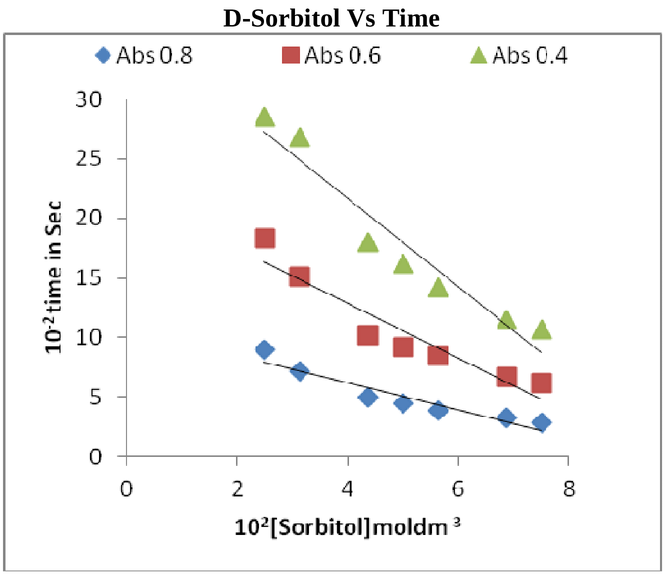
D-Mannitol Vs Absorbance



A_6 = - 0.039[D-Mannitol]+ 0.942 Corr. Coeff. = 0.98
A_{12} = - 0.059[D-Mannitol]+ 0.905 Corr. Coeff. = 0.98
A_{18} = - 0.067[D-Mannitol]+ 0.759 Corr. Coeff. = 0.97
Result: 10^2[Unknown-1](moldm^{-3}) = 3.77(calcd.): 3.75(actual)
10^2[Unknown-2](moldm^{-3}) = 6.24(calcd.): 6.25(actual)

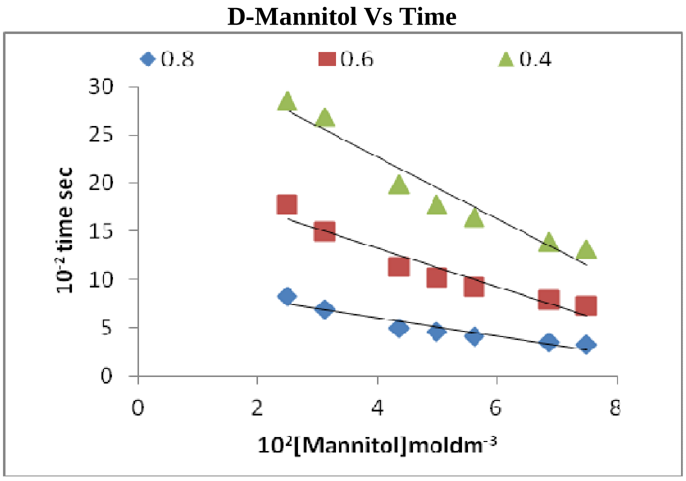
(b) Estimation of D-Mannitol

Fig.2 Estimation of alditols by variation of absorbance at fixed time. $10^4[Ce^{IV}]$ = 2.5 moldm^{-3}; $[H_2SO_4]$ = 0.7moldm^{-3}; Temp.= 296K ; λ = 360nm.



$t_{0.8}$ = - 1.144[D-Sorbitol]+10.63 Corr. Coeff. = 0.90
$t_{0.6}$ = - 2.316[D-Sorbitol]+21.88 Corr. Coeff. = 0.90
$t_{0.4}$ = - 3.72[D-Sorbitol]+36.28 Corr. Coeff. = 0.93
Result: 10^2[Unknown-1](moldm^{-3}) = 3.8(calcd.): 3.75(actual)
10^2[Unknown-2](moldm^{-3}) = 6.23(calcd.): 6.25(actual)

(c) Estimation of D-Sorbitol



$t_{0.8}$ = - 0.956[D-Mannitol]+9.88 Corr. Coeff. = 0.90
$t_{0.6}$ = - 2.012[D-Mannitol]+20.8 Corr. Coeff. = 0.92
$t_{0.4}$ = - 3.190[D-Mannitol]+35.45 Corr. Coeff. = 0.94
Result: 10^2[Unknown-1](moldm^{-3}) = 3.78(calcd.): 3.75(actual)
10^2[Unknown-2](moldm^{-3}) = 6.25(calcd.): 6.25(actual)

(b)Estimation of D-Mannitol

Fig.3 Estimation of alditols by variation of time at fixed absorbance. 10^4[Ce^{IV}] = 2.5 moldm^{-3}; [H_2SO_4] = 0.7moldm^{-3}; Temp.= 296K ; λ = 360nm.

The graphical data has been used to obtain unknown concentration of simulated samples of alditols using regression equations in respective graphs.The results of the estimation with actual theoretical values are also given in respective figures.

CONCLUSION

The popularity of reaction rate method in chemical analysis is indicated by the variety of methodologies that have been developed and appeared in many review articles and research papers as well as in some book. The above method proposed is simple & accurate, hence the above method can be used for estimation of alditols in industry and for laboratory experiments at college level.

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